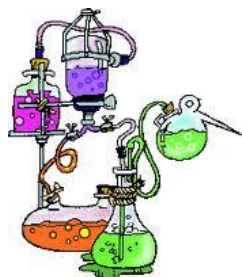


# *Supramolecular Chemistry for Pressure Sensitive Adhesives ?*

*Adhesion Society Meeting 2013*

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MATEIS, INSA, Lyon, France



## PSA = Pressure Sensitive Adhesives



A soft material which sticks on almost any surface by simple contact, without chemical reaction

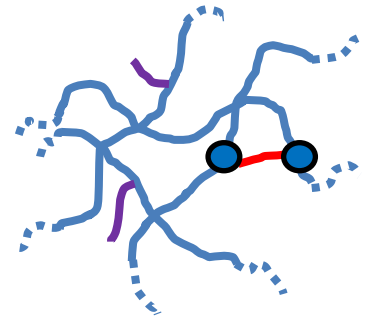


A PSA is **viscoelastic** and it sticks thanks to its **rheological** properties

Entanglements  $\longrightarrow$  Viscoelasticity

### Classical Chemistry for Acrylic PSA

Entangled polymer chains with pendant chains and a low cross-linker density



Challenge :

Is it possible to get a viscoelastic behavior required for a PSA with **unentangled molecules** with **strong** but **reversible** interactions ?



High solubility in classic organic solvent

In solution, viscosity would be much lower compared to entangled polymers solution.

What is required ?

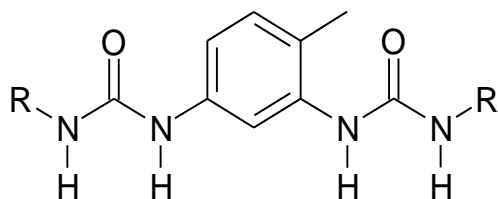
Strongly interacting moieties separated by flexible polymer chains.



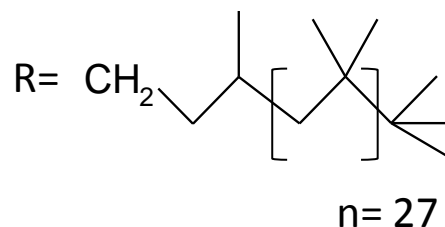
Supramolecular Polymer

Origin of the project : **Pibut** Poly(isobutene) Bis-Urea Toluene ( $M_w \approx 3\,000\text{g/mol}$ )

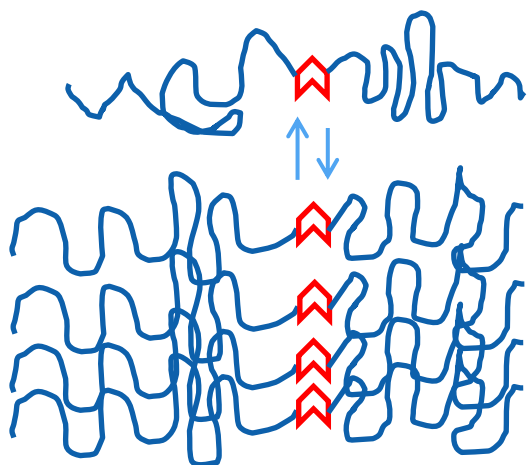
Courtois et al, *Adv. Funct. Mater.* **2010**, 20, 1803-1811



Polar core



Linear Pib Chain

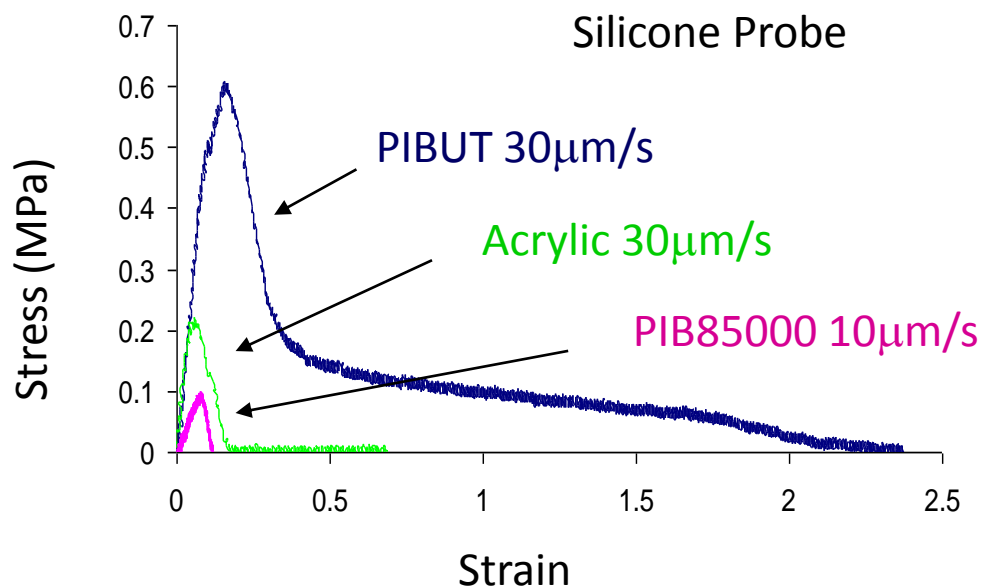


H-Bond interactions  
Self-assembling of the cores

Soft viscoelastic gel  $G' \approx 10^4$  Pa at RT  
Structured Material  $d^* \approx 4\text{nm}$  at SAXS, RT

Origin of the project : **Pibut** Poly(isobutene) Bis-Urea Toluene ( $M_w \approx 3\,000\text{g/mol}$ )

Courtois et al, *Adv. Funct. Mater.* **2010**, 20, 1803-1811



Pibut showed unexpected adhesive properties on silicone !!

## Question

Does supramolecular structure improve the adhesive properties on Silicone ?

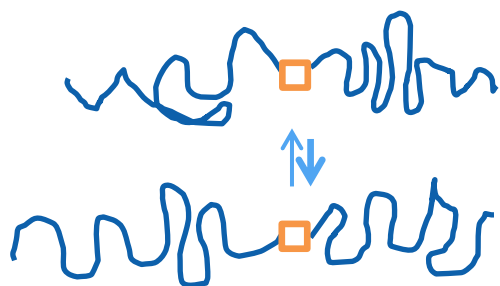
Is this effect only due to the Pibut rheological properties ?



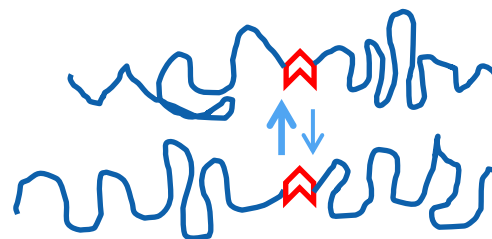
## Strategy

Influence of the supramolecular parameters on rheology, structure and adhesion.

1. **Level of interactions** : the nature of the polar core.



Weak interactions

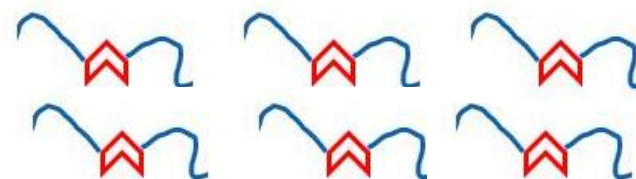


Strong interactions

2. **the interacting moieties density** : the size of the linear non polar chains

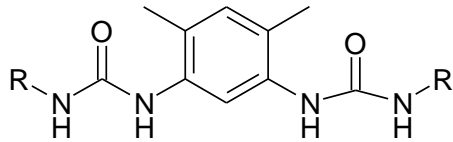


Low polar core concentration

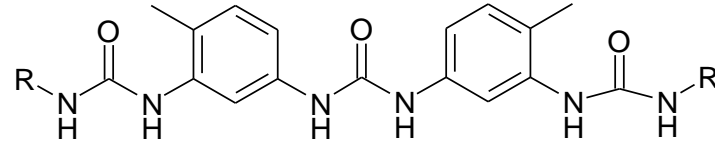


High polar core concentration

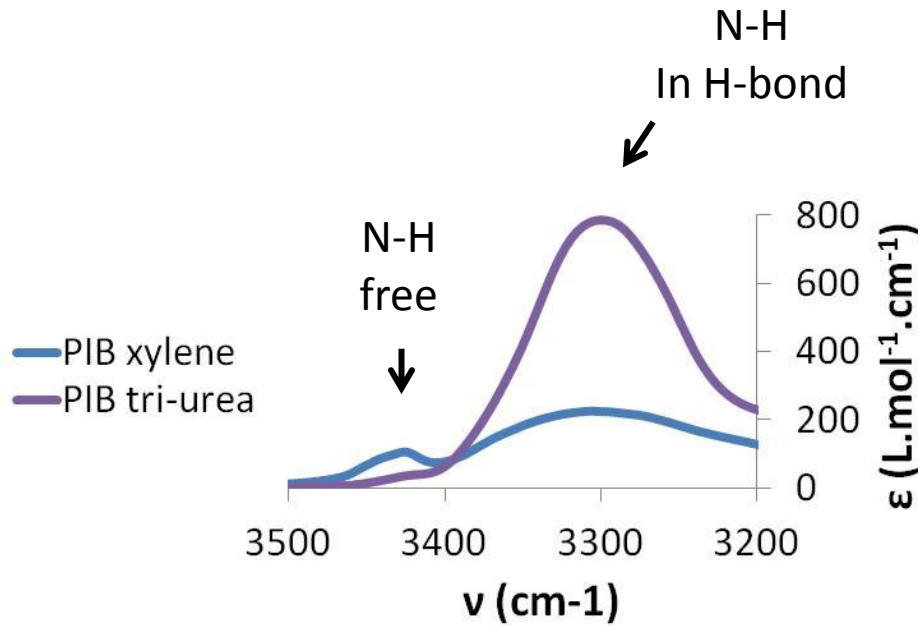
## Chemistry of the Polar cores



Bis-urea Xylene



Tri-Urea Toluene



FTIR Spectra in CHCl<sub>3</sub> at 4mM

Interactions  
Bis-Urea Xylene << Tri-Urea Toluene



# Chemistry of the Side Chains

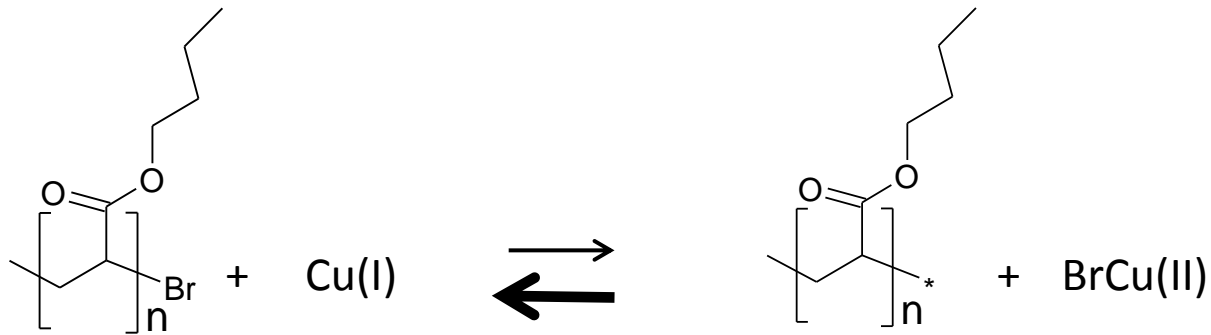


~~Polyisobutene~~



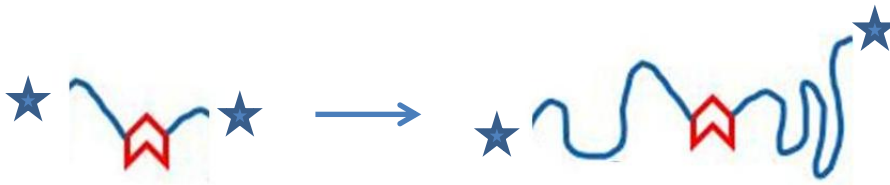
Polybutylacrylate

Atom transfer radical polymerization (ATRP)



Non Living Chains

Living Chains



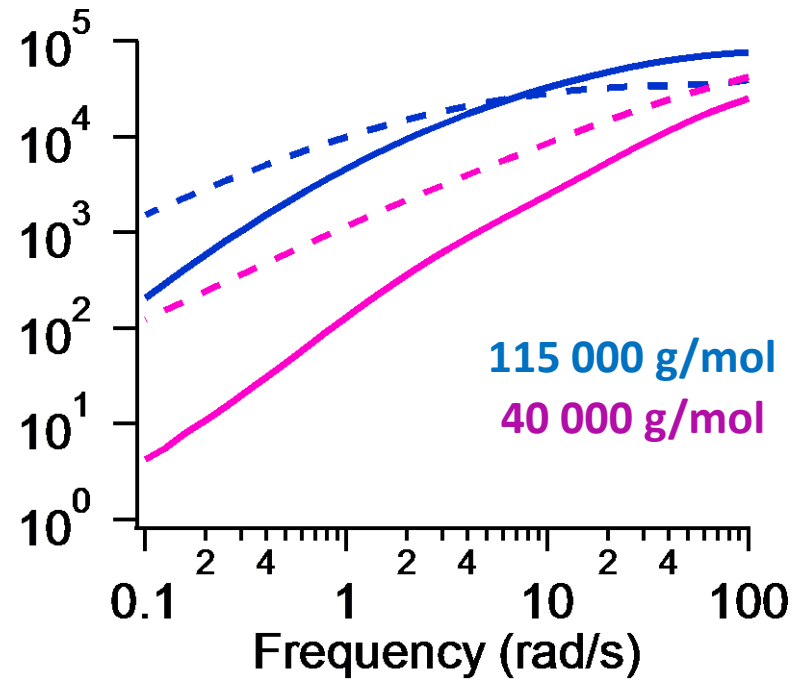
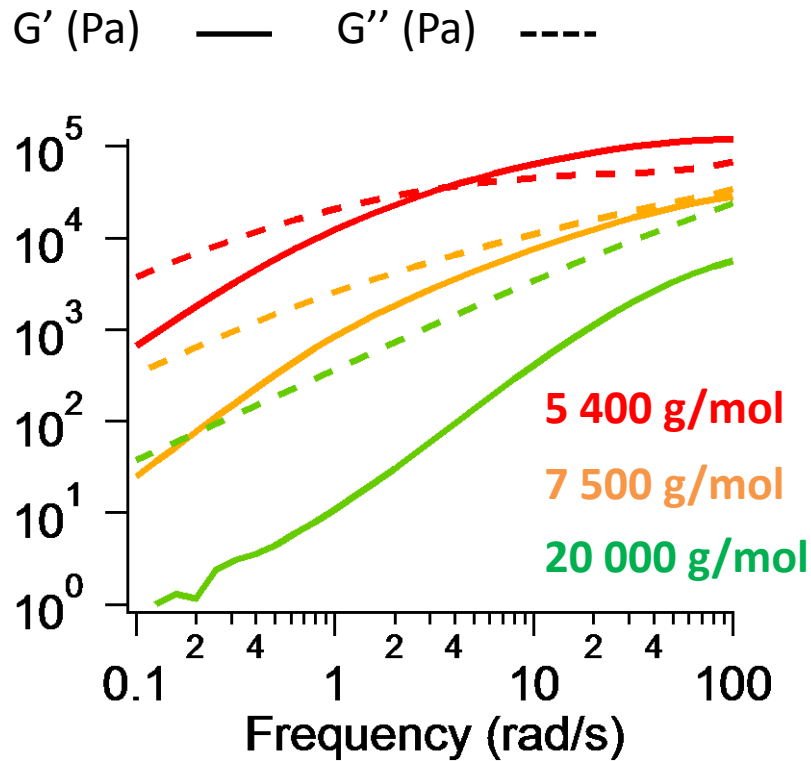
In the two families :  
5 000 g/mol < Mw < 115 000 g/mol



# Supramolecular Polymers with **weak** interactions

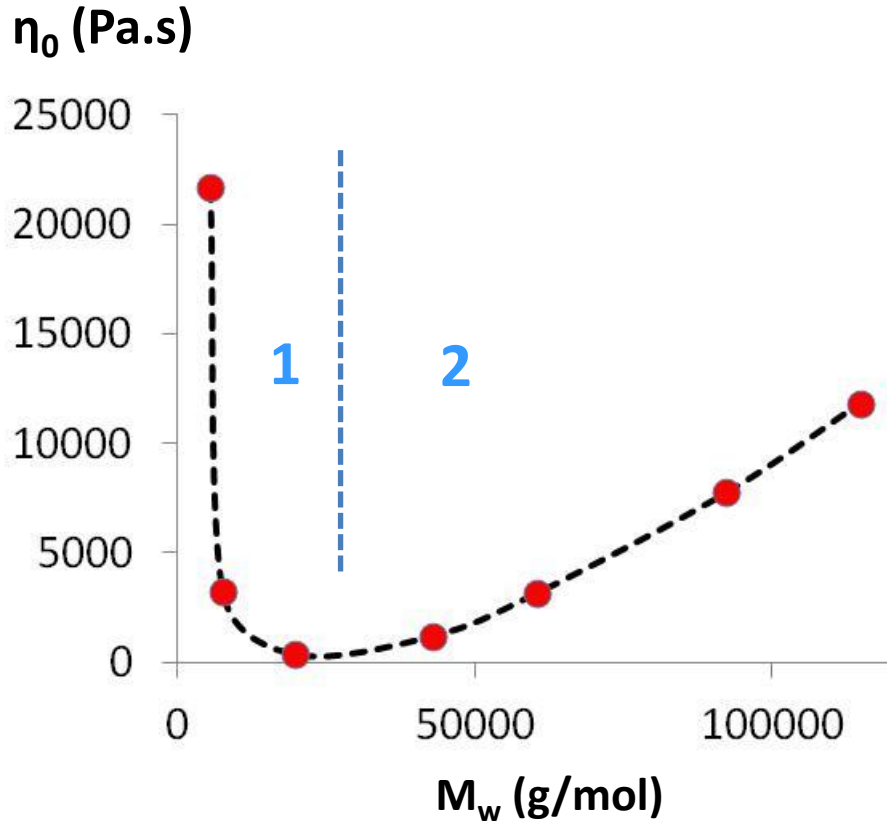
Viscoelastic behaviors are observed at low and high molecular weight.

At intermediate molecular weights, polymers are viscous liquid.



Frequency sweep at small strain (1-10%).  $T = 25^\circ\text{C}$ .

Newtonian Fluid at low frequency,  $\eta \neq f(\omega)$



Regime 1

$\eta_0$  increases with the polar core density

H-bond  $\longrightarrow$  Viscoelastic

Regime 2

$\eta_0$  increases with  $M_w$

Entanglement  $\longrightarrow$  Viscoelastic

H-Bond  $\approx$  Entanglement

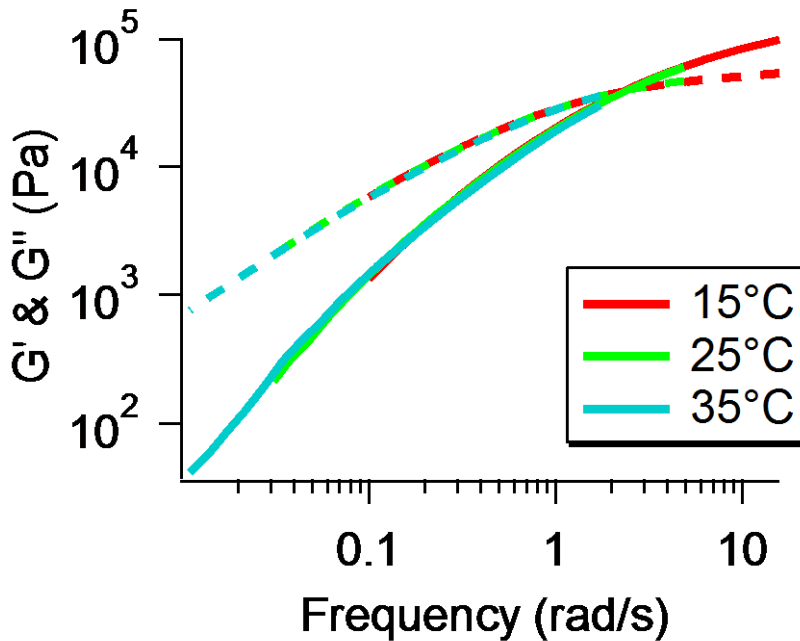


Our supramolecular polymers still flows

H-Bond  $\neq$  Cross-linker

No peak is observed at SAXS

No permanent structure like Pibut



Master Curve :

No temperature dependent structure

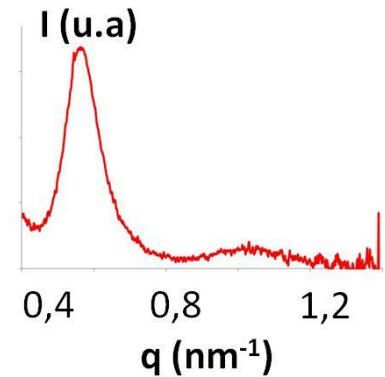
Frequency Sweep for 5 400g/mol,  $\gamma < 10\%$

# Supramolecular Polymers with **strong** interactions ( $M_w \leq 40\,000$ g/mol)

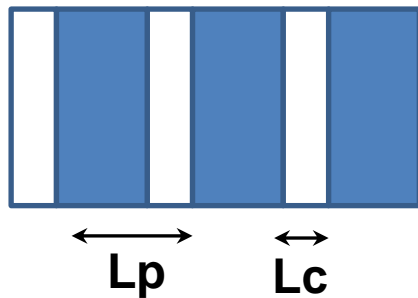


A peak is observed at SAXS for low molecular weight !

→ Permanent structure like Pibut !!

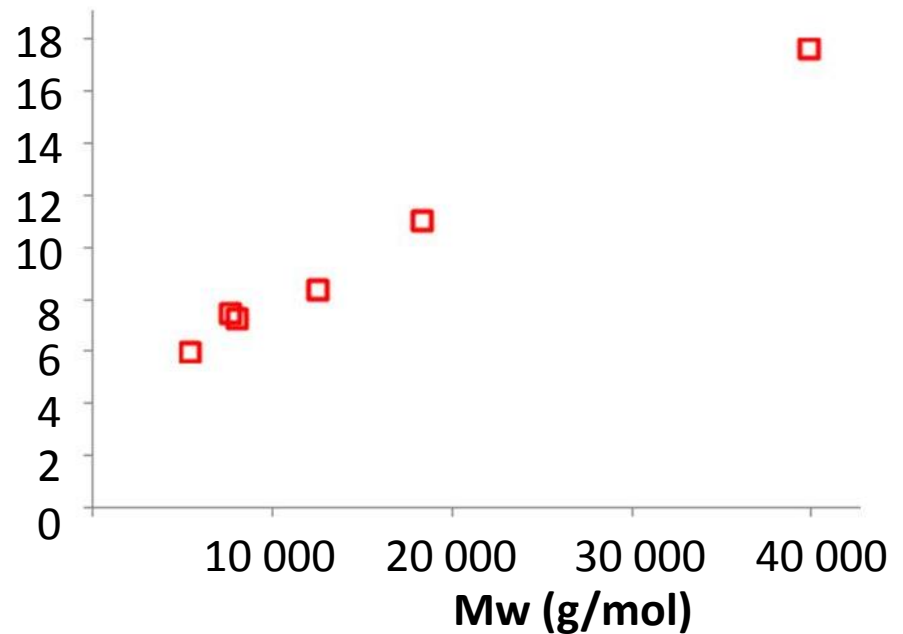


A lamellar structure is proposed



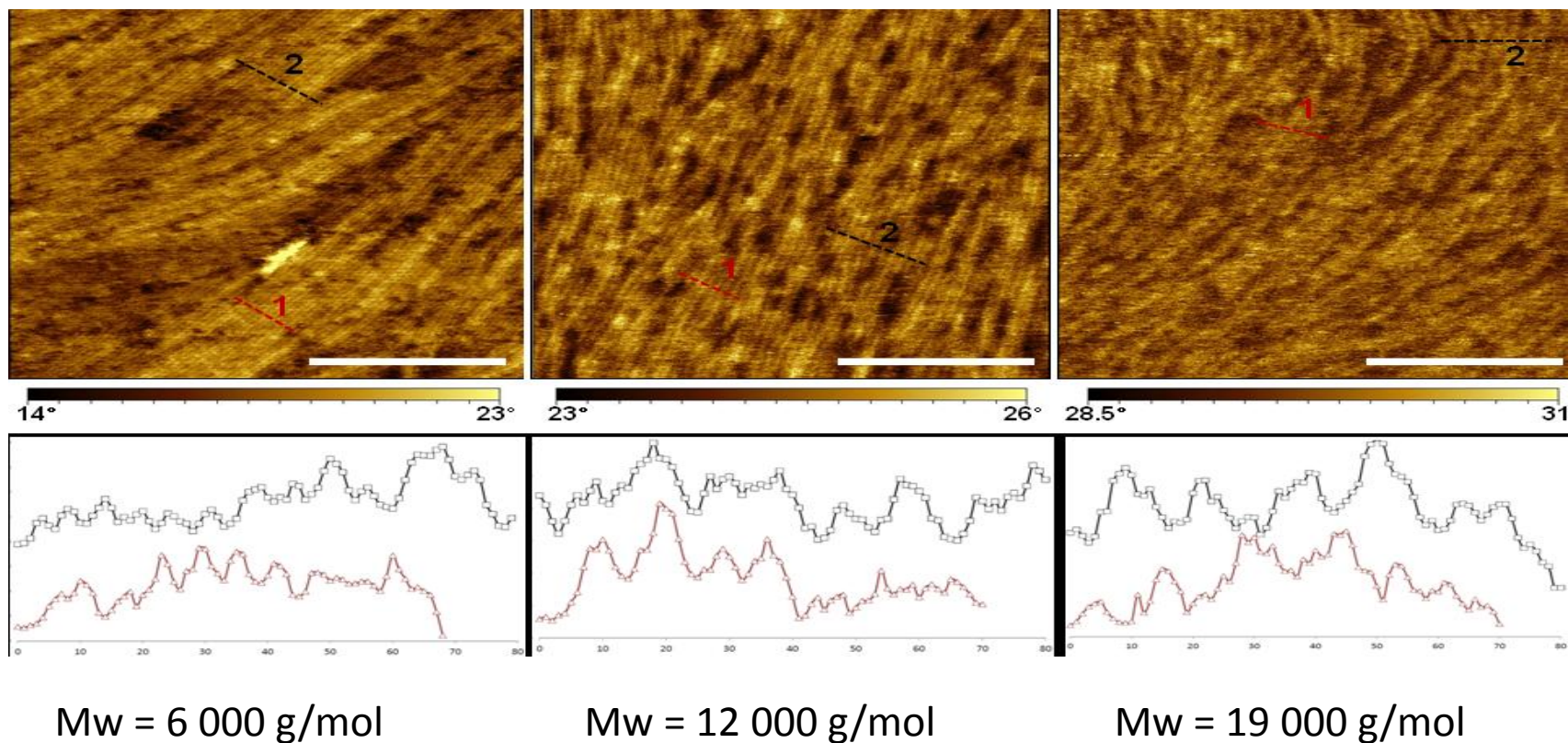
$$L_p = L_c / f_c \rightarrow L_p \propto M_w$$

Bragg Distance (nm)



# Supramolecular Polymers with **strong** interactions ( $M_w \leq 40\,000$ g/mol)

The structure was confirmed by Atomic Force Microscopy (AFM)

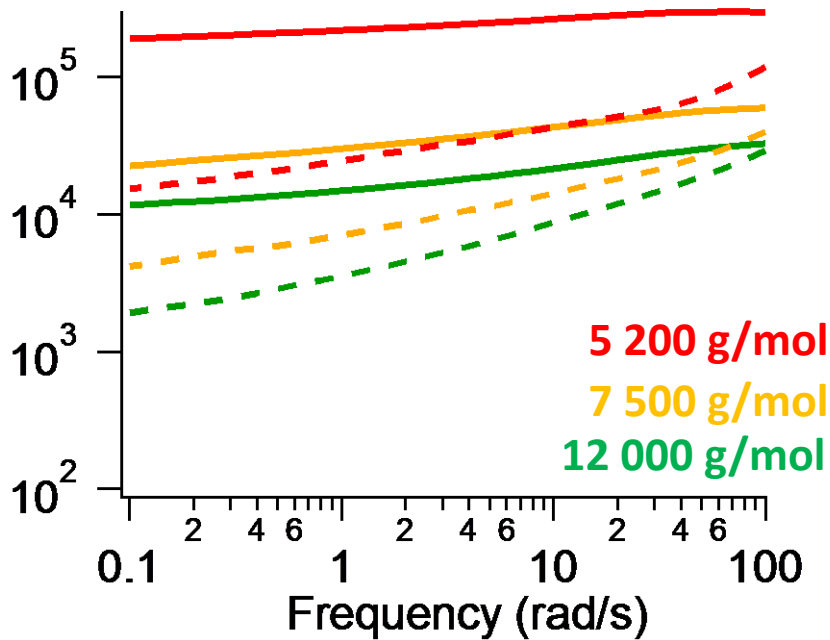


# Structured Supramolecular polymers : $M_w \leq 40\ 000\ \text{g/mol}$

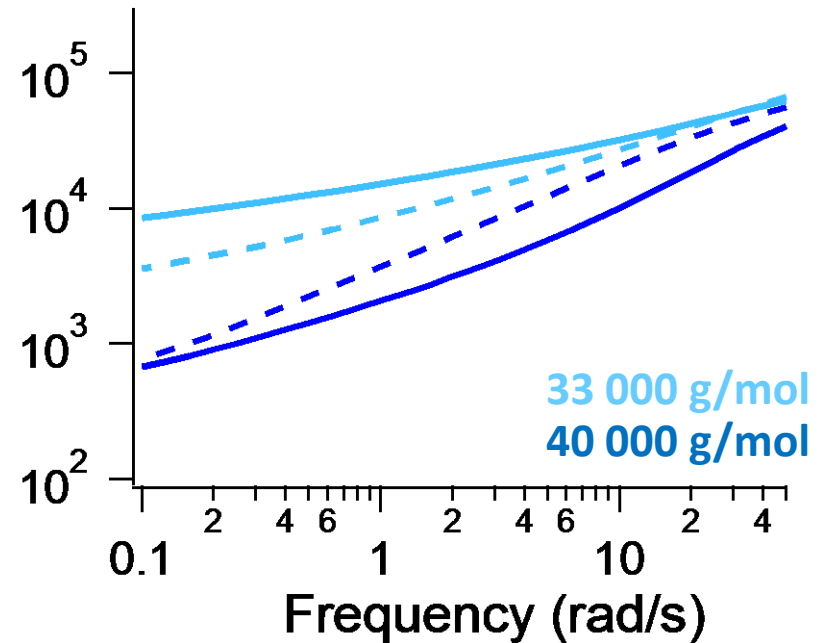


Supramolecular polymers don't flow at low molecular weight !

At low  $M_w$ ,  
elastic Gel



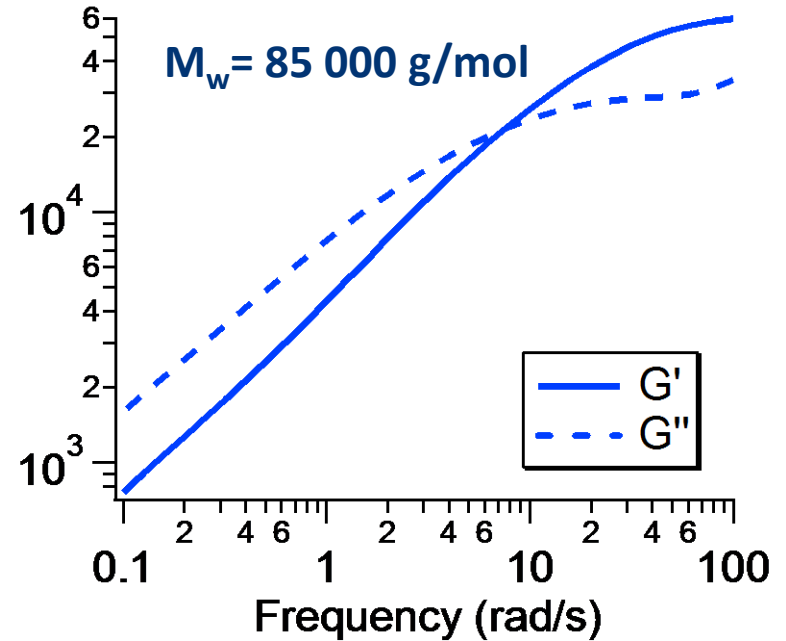
At intermediate  $M_w$   
viscoelastic Gel



$G'$  (Pa) —  $G''$  (Pa) T=25°C

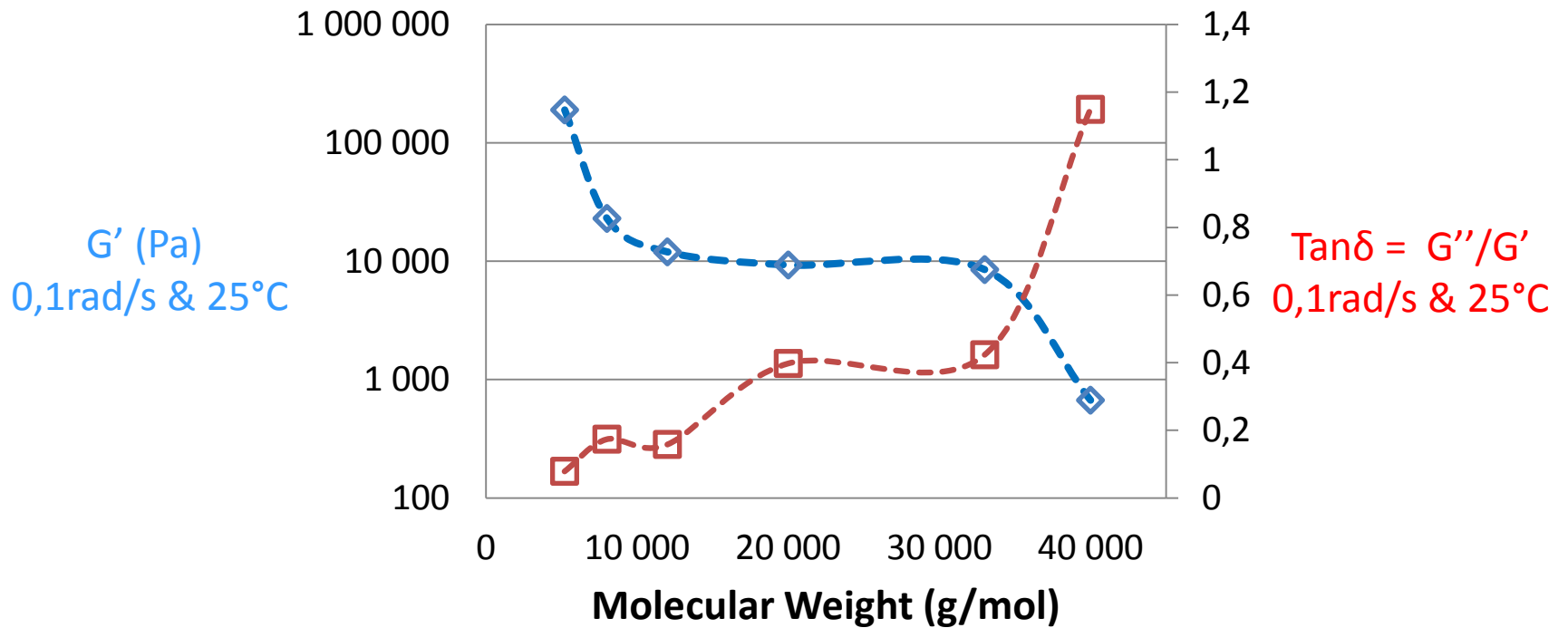
Supramolecular Polymers with  
**strong** interactions :  $M_w \geq 40\,000$  g/mol

{ No structure observed at SAXS  
Viscoelastic Fluid



At low Molecular weight = high sticker density

Self assembly of the polar core  $\rightarrow$  Structure observed at SAXS  $\rightarrow$  Non flowing material



Strong H-Bond  
Interactions



Similar rheology than for  
commercial Adhesives

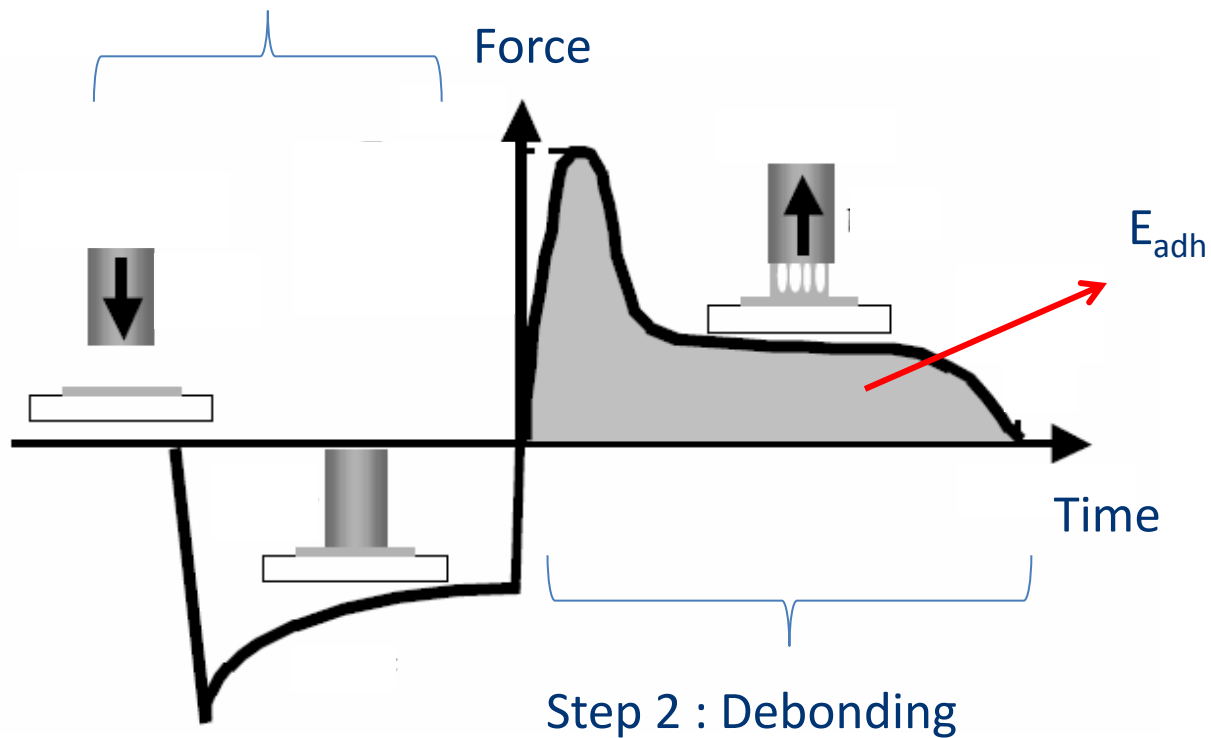




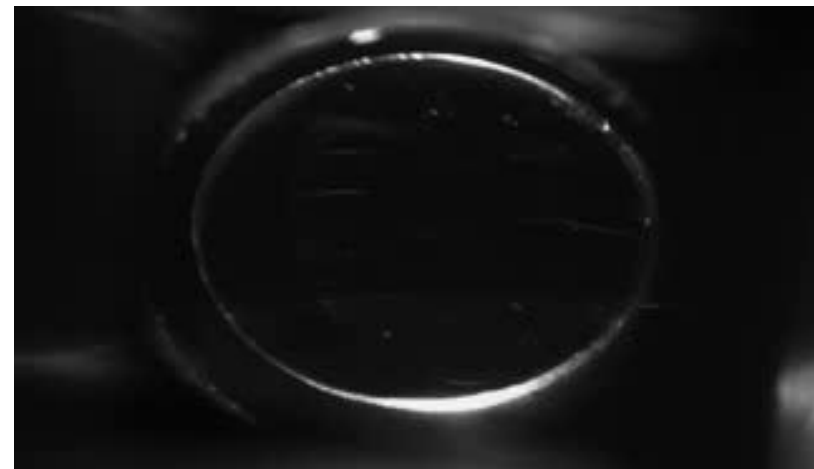
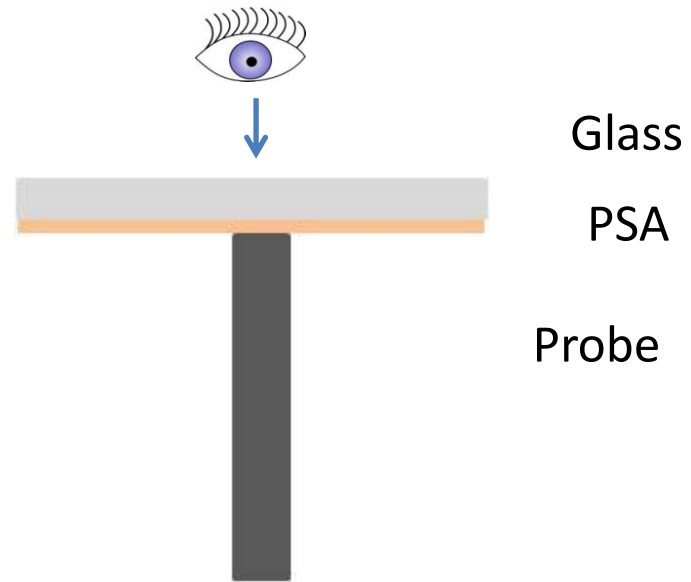
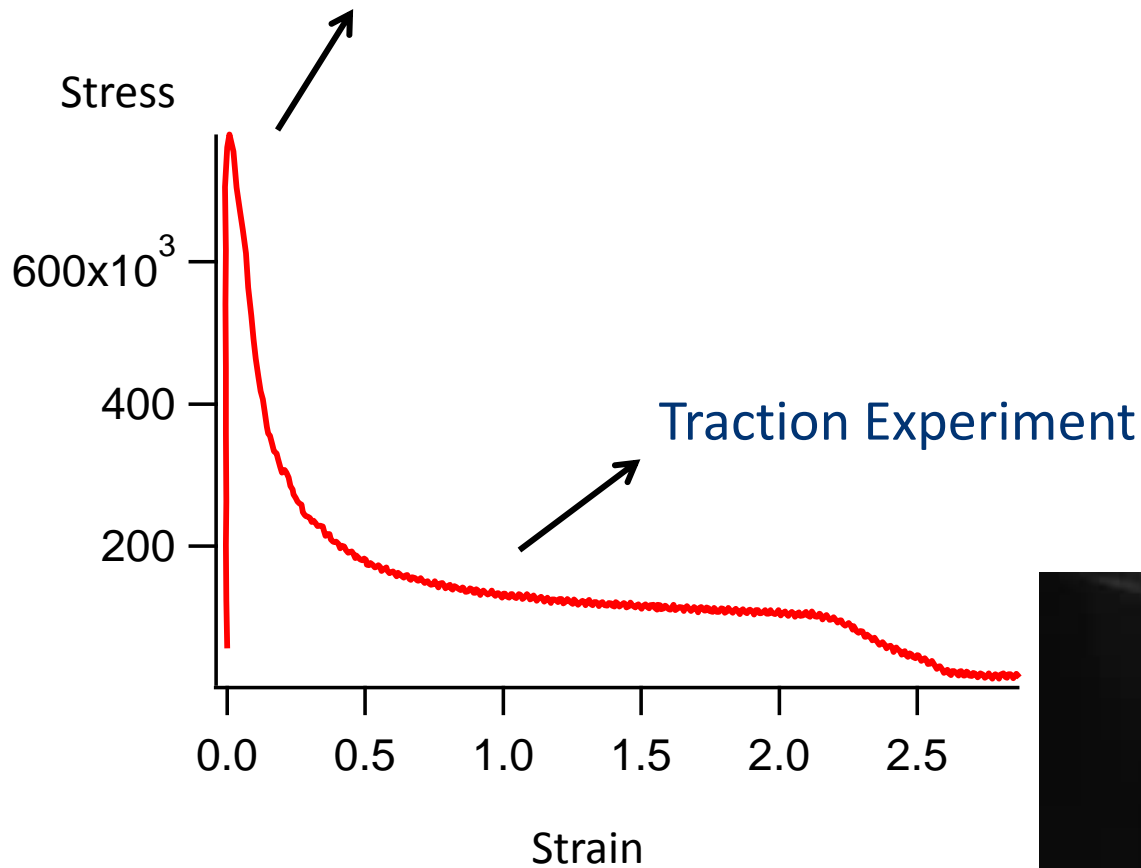
# Probe-tack Experiments

## Flat punch

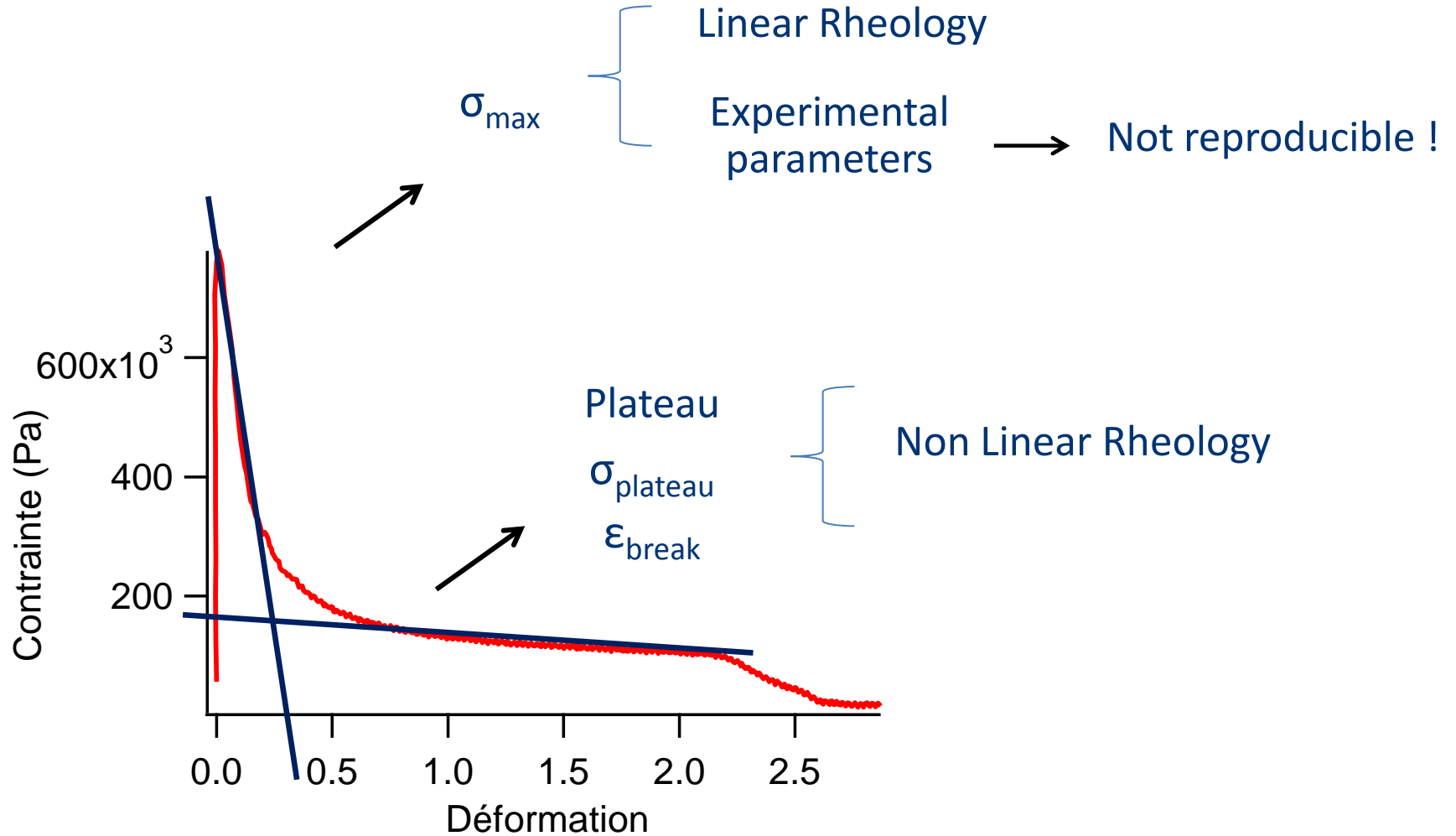
Step 1 : Contact



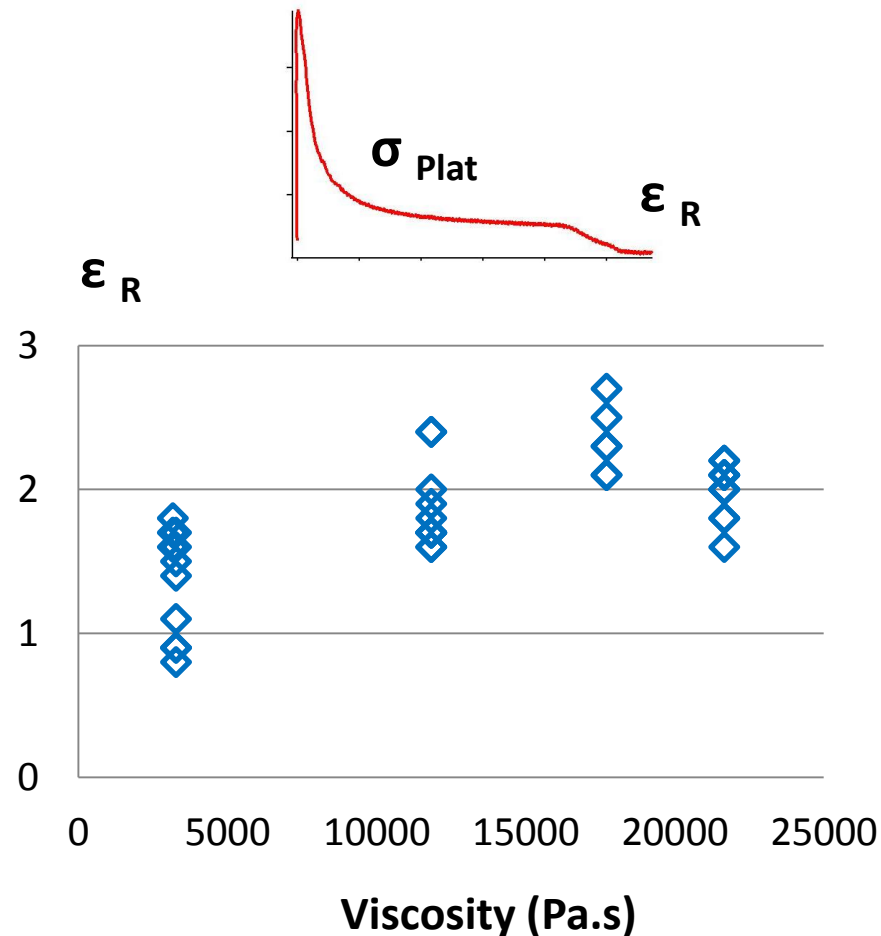
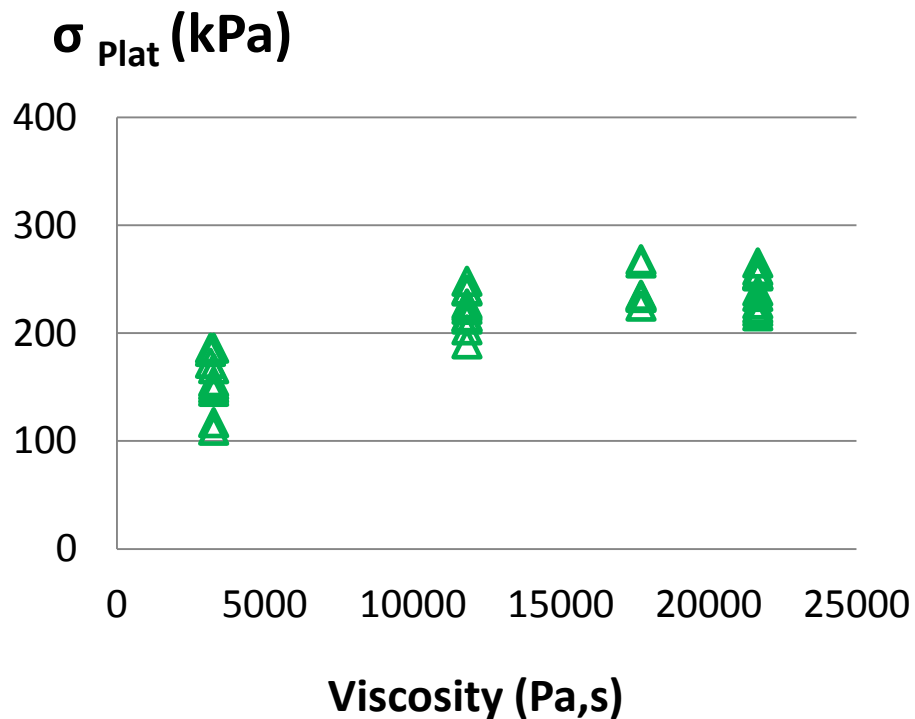
## Cavitation Process



# Probe-tack Experiments



# Flowing and disordered Supramolecular polymers

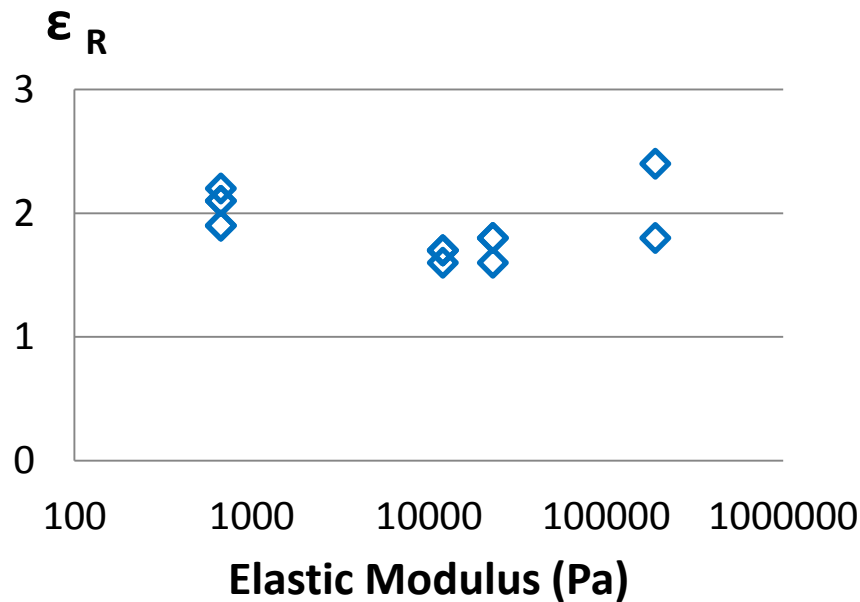
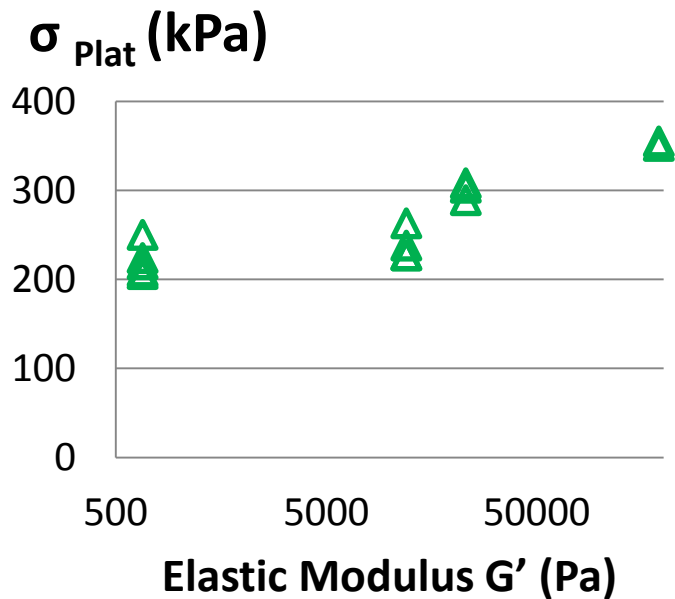
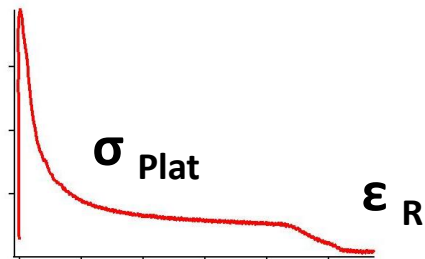



H-bond interactions increase  
the viscosity of low  $M_w$  polymers.



Increase of Energy adhesion of  
low  $M_w$  by H-bonds interactions

# Non Flowing and ordered Supramolecular polymers




 {  $\epsilon_R$  &  $\sigma_{plat}$  is similar for all samples  
 Cohesive Rupture like liquids.

Softening mechanisms at high strain ??

Supramolecular polymer  $\approx$  Yield Stress Fluid

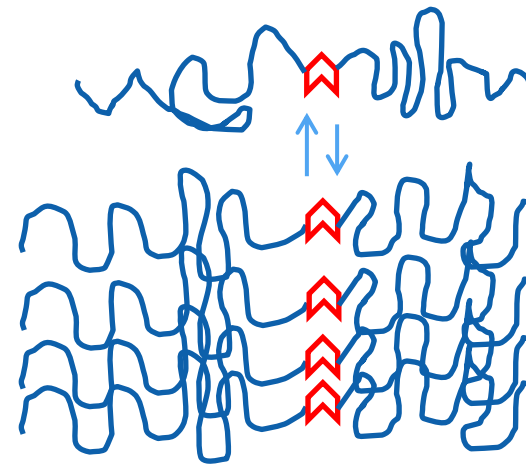
# Conclusion

Is-it possible to get the PSA-like properties with small functionalized molecules ?

Self assembly of the polar molecules

Structure

Soft Viscoelastic gel



## Promising rheological results at small strain

Sticky material but liquid-like behavior for adhesion !

↳ Work on new molecular architecture

*Thank you to :*

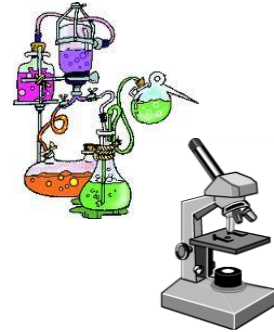
*Scientists involved in Supradhesion :*



**Cécile Fonteneau, Sandrine Pensec, Laurent Bouteiller**



**Cyril Véchambre, Jean-Marc Chenal, Laurent Chazeau**

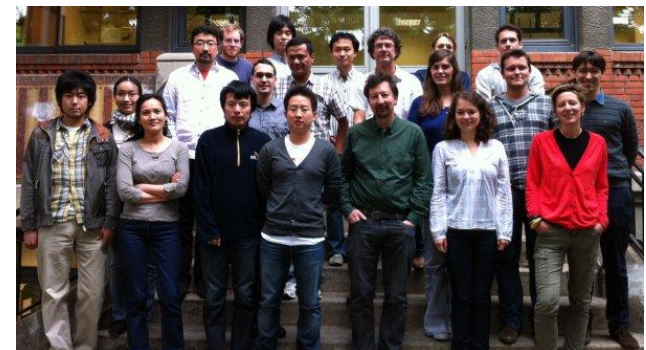


***CNRS & ANR Project for Financial Support***

***PPMD/SIMM for Technical Support***



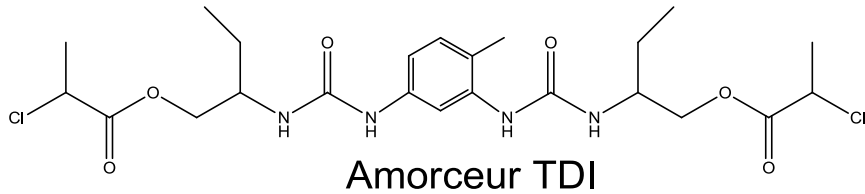
*The Soft Polymer Network team :  
Costantino, Guylaine, Chelsea, Ludovic,  
François, David...*



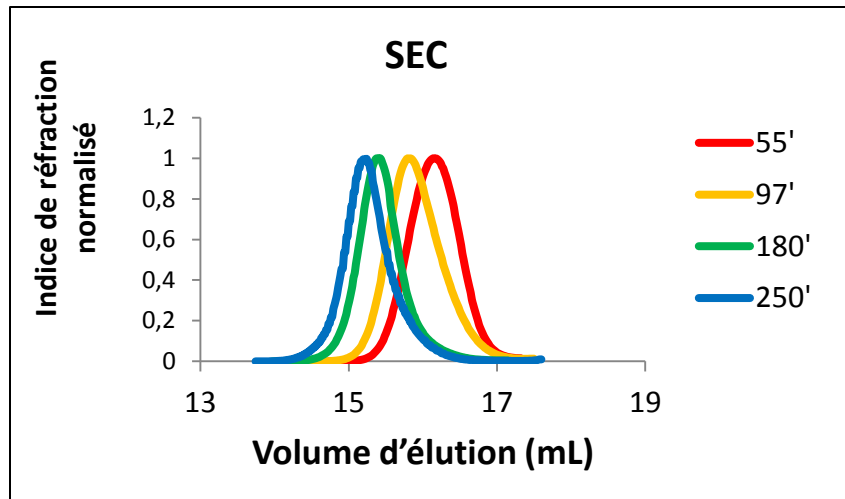
*Thank you for attention !!*



# Cinétique de polymérisation : exemple de l'amorceur coeur TDI

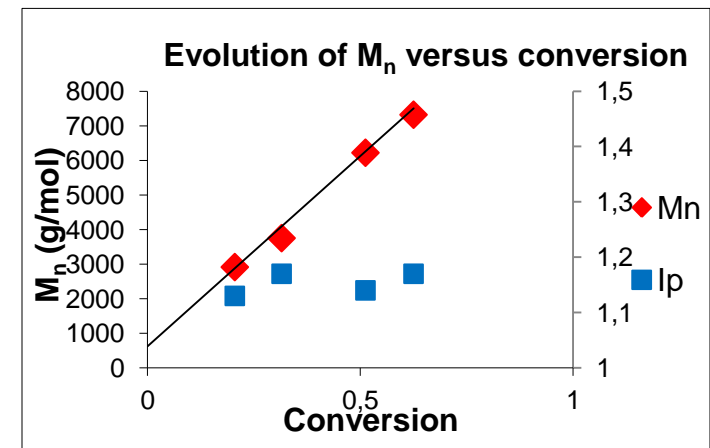
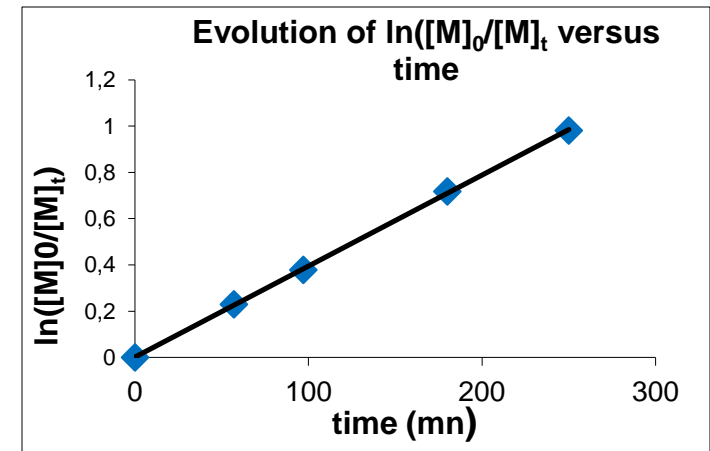


$[ABU]/[A]/[CuCl]/[PMDETA] = 86 / 1 / 1 / 1$   
 dans 10% DMF, 80°C



Cinétique de premier ordre linéaire

Evolution linéaire de  $M_n$  en fonction de la conversion



### Infrarouge pABu à 1mM dans le toluène

3410 $\text{cm}^{-1}$  : NH  
liés aux esters

3450 $\text{cm}^{-1}$  : NH  
libres

3360 $\text{cm}^{-1}$  : NH liés inter urées

3300 $\text{cm}^{-1}$  : NH liés  
inter urées

